III.A.18 Cathodes for Low-Temperature SOFC: Issues Concerning Interference from Inert Gas Adsorption and Charge Transfer

Anil V. Virkar
University of Utah
Department of Materials Science & Engineering
122 S. Central Campus Drive
Salt Lake City, UT 84112
Phone: (801) 581-5396; Fax: (801) 581-4816; E-mail: anil.virkar@m.cc.utah.edu

DOE Project Manager: Lane Wilson
Phone: (304) 285-1336; E-mail: Lane.Wilson@netl.doe.gov

Objectives

- To synthesize dense samples of perovskite mixed ionic electronic conductors (MIECs), including Sr-doped $LaMnO_3$ (LSM) (which is predominantly an electronic conductor with negligible ionic conductivity), Sr-doped $LaCoO_3$ (LSC) and Sr-doped $LaFeO_3$ (LSF).
- To investigate oxygen incorporation reaction by the proposed electrochemical method using mixtures of O_2 and N_2, as well as of O_2 and Ar.
- To fabricate anode-supported cells with MIEC + yttria-stabilized zirconia (YSZ) or MIEC + Sm-doped ceria (SDC) composite cathodes.
- To investigate cell performance and cathodic polarization as a function of temperature and composition of the oxidant.

Approach

- Synthesize LSM, LSC, and LSF powders by conventional methods as well as by combustion synthesis.
- Fabricate dense and porous samples of LSM, LSC, and LSF by pressing and sintering.
- Investigate oxygen exchange kinetics using the conductivity relaxation method.
- Fabricate patterned electrodes and measure charge transfer resistance as a function of three-phase boundary (TPB) length.
- Investigate the dependence of cell performance on oxygen partial pressure by using oxidants containing various mixtures of O_2 and an inert gas.

Accomplishments

- A new method of analysis was developed for the conductivity relaxation technique which facilitates the determination of the surface exchange coefficient and chemical diffusion coefficient.
- Using patterned electrodes of LSM on YSZ, it was demonstrated that the oxygen reduction reaction predominantly occurs at the TPB. Using this technique, charge transfer resistivity was measured as a function of temperature and oxygen partial pressure.
- Single cells were tested in various $O_2 + N_2$, O_2 + Ar, and $O_2 + CO_2$ gas mixtures.
- In 100% O_2 as oxidant and at 800°C, maximum power density as high as ~2.9 W/cm^2 was demonstrated.

Future Directions

The funded project has been completed, and no more work is planned. However, the following work is necessary for full evaluation of the proposed concept.

- Conduct experiments on the measurements of oxygen exchange coefficients and chemical diffusion coefficients on LSM, LSF, and LSC.
- Investigate the role of adsorption using patterned electrodes of LSF and LSC on YSZ and on other electrolytes such as ceria and Sr- and Mg-doped $LaGaO_3$ (LSGM).
- Investigate the role of chromium on the cathodic reaction using patterned electrodes.

Introduction

Typical oxidant in the operation of a solid oxide fuel cell (SOFC) is air, which contains 21% oxygen. When an SOFC is operating at a finite, nonzero current density, the oxygen content (partial pressure) close to the cathode/electrolyte interface is lower than that in pristine air. Also, when a stack is operated, the oxidant becomes depleted in oxygen, thus further lowering the oxygen content. In such cases, the oxygen content close to the cathode/electrolyte interface can be very low – perhaps approaching 2 to 4%, which means nitrogen is the predominant species at the cathode/electrolyte interface, where the cathodic reaction occurs. Low concentration of oxygen is expected to lead to low electrochemical reaction rate and lower performance. Under such conditions, the possible relative adsorption of nitrogen needs to be considered. Alternatively, regardless of the possible adsorption of nitrogen, relative decreased adsorption of oxygen needs to be taken into consideration. What is desired is a cathode material which preferentially adsorbs oxygen, thereby increasing the exchange current density.

The objective of this work was to investigate fundamental parameters that dictate cathodic charge transfer reaction rates of MIEC cathodes. This entailed investigation of the surface exchange coefficient and chemical diffusion coefficient of oxygen. In cathodes, which are predominantly electronic conductors such as LSM, the electrochemical reaction is expected to occur at the TPB. Investigation of the electrochemical reaction rate with such cathodes was conducted using patterned electrodes made by photo micro lithography. Finally, anode-supported button cells were made and tested in oxidants containing various oxygen concentrations.

Approach

Samples of MIEC materials such as LSC and LSF were fabricated as bars, both in a fully dense as well as a porous form. The surface exchange coefficient was measured by the conductivity relaxation technique as a function of temperature and partial pressure of oxygen. Discs of yttria-stabilized zirconia were formed. Patterned LSM electrodes were deposited using photo micro lithography. The TPB was varied over a wide range, between 50 and 1200 cm^{-1}. Impedance spectra were obtained over a range of temperatures and oxygen partial pressures. Anode-supported button cells with Ni + YSZ anode, YSZ electrolyte and LSM + YSZ or LSC + SDC cathode were made. The cells were tested at 800°C with hydrogen as fuel and an oxidant containing various concentrations of oxygen.

Results

Figure 1 shows experimentally measured surface exchange coefficient as a function of oxygen partial pressure between ~0.02 and ~0.21 atm at 800°C on LSC using a porous sample. Note that the surface exchange coefficient increases with increasing oxygen partial pressure and then levels off, consistent with adsorption as a dominant step. Figure 2 is a scanning electron micrograph (SEM) of a patterned LSM electrode on a YSZ disc. The TPB was varied over a wide range by using different masks. On each disc, a counter electrode was deposited on the opposite face, and a reference electrode was wound along the cylindrical surface. Impedance spectra were measured over a range of temperatures and oxygen partial pressures. Figure 3 is an example of impedance spectra obtained. In this case, the impedance spectra were obtained on a sample of TPB length corresponding to 1200 cm^{-1} as a function of oxygen partial pressure at 800°C. The intercept of the semi-circular arc on the x-axis gives the net charge transfer resistance. Note that as the oxygen partial pressure is increased, the charge transfer resistance decreases. Figure 4 shows the results of cell performance tests at 800°C using an anode-supported cell with LSC + SDC cathode. Note that power density as high as ~2.9 W/cm^2 could

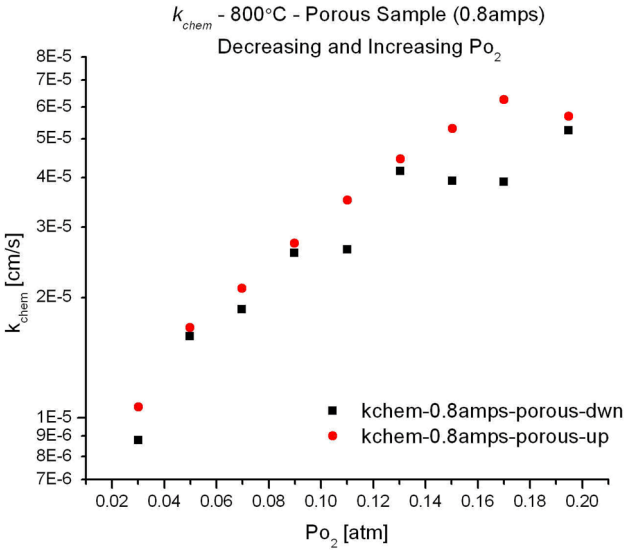

Figure 1. Plots of k_{chem} vs. PO_2 at 800°C, during both increasing and decreasing PO_2, measured using porous sample. Note that at low values of PO_2, the k_{chem} is virtually the same either during increasing PO_2 or decreasing PO_2. The variance at high PO_2 may be experimental scatter. Note that k_{chem} increases with increasing PO_2. It is anticipated that at high PO_2, it will plateau out, consistent with Langmuir type adsorption.

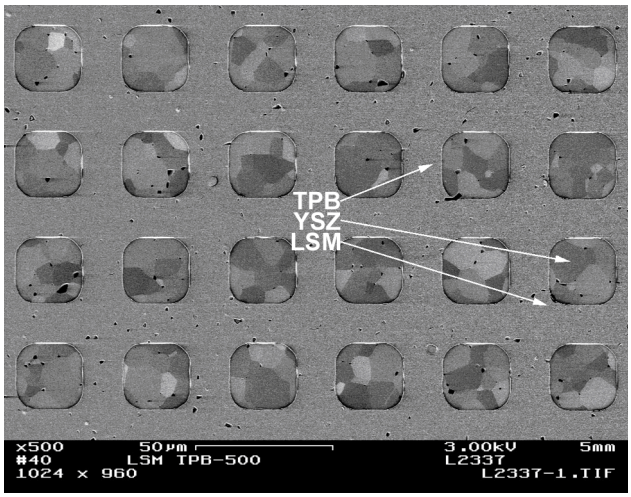

Figure 2. An SEM image of LSM patterned electrode deposited on a YSZ disc (deposited using the facilities at Pacific Northwest National Laboratories). The square regions are of YSZ, in which the grains can be seen. The rest of the region is the LSM coating. The l_{TPB} of this sample is 500 cm^{-1}.

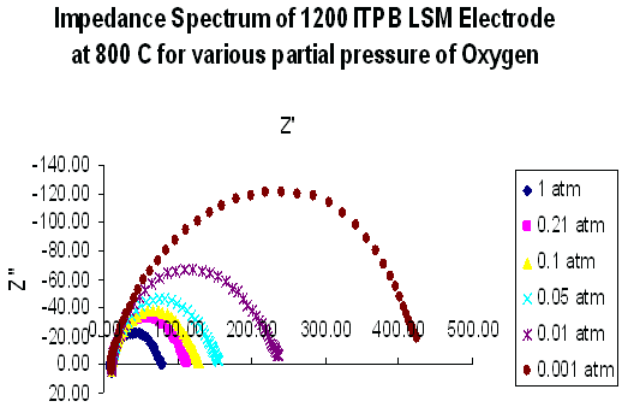

Figure 3. Impedance spectra on LSM patterned electrodes as a function of partial pressure of oxygen, PO_2, in O_2-N_2 gas mixtures as oxidant.

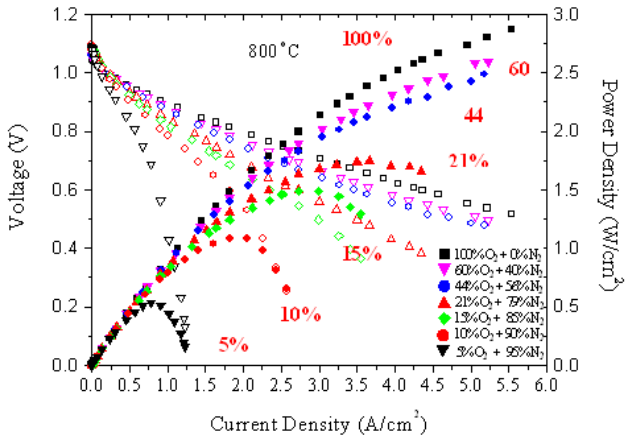

Figure 4. Voltage and power density vs. current density plots for a cell in oxidants of various compositions, ranging between ~5% O_2 + 95% N_2 to ~100% O_2. Fuel: Hydrogen. Temperature: 800°C.

be achieved in pure oxygen. However, in an oxidant containing ~5% O_2 + ~95% N_2, the power density is about 0.5 W/cm^2. A large part of the decrease at high nitrogen concentration is related to the high charge transfer resistance at low oxygen concentrations. This result underscores the importance of investigating adsorption effects.

Conclusions

The principal objective of the work was to demonstrate the effects of oxygen content in the oxidant on parameters which determine cathodic

activity, namely surface exchange coefficient of MIEC materials and charge transfer resistance with predominantly electronic conductors as cathodes. These properties were investigated on LSC and LSM electrodes, respectively. The studies showed that both the surface exchange coefficient and charge transfer resistance are dependent on oxygen partial pressure. Single cells made and tested also showed that the performance increases with increasing oxygen partial pressure. The present work demonstrates a direct relationship between oxygen content and cathodic activation polarization and explores its implications in governing cell performance. Power density as high as ~2.9 W/cm^2 at 800°C was demonstrated.

FY 2004 Publications/Presentations

1. "Estimation of Charge Transfer Resistivity of $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ (LSM) Cathode on $Y_{0.16}Zr_{0.84}O_{2-\lambda}$ (YSZ) Using Patterned Electrodes", R. Radhakrishnan, A. V. Virkar, and S. C. Singhal; accepted for publication in the Journal of the Electrochemical Society (2004).